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AN IMPROVED METHOD OF MAKING BORDEAUX MIXTURE.

By W. T. SWINGLE.

Since the first of the year I have had under way rather extensive experiments with Bordeaux mixture to determine its effectiveness in preventing a fungous disease of the lemon known as scab. The necessity of making large quantities of the mixture soon showed how slow and inefficient the common methods for its preparation are. After a number of attempts a much quicker and at the same time better method was worked out, and it is the object of this paper to call attention to the method. It might be noted that the lemon proves to be exceedingly sensitive to slight changes in the composition of the mixture, and hence is a very good plant to use in determining the best form of this fungicide.

METHODS OF DISSOLVING THE COPPER SULPHATE.

Probably the best method of dissolving large quantities of copper sulphate without heat is that suggested by Mr. M. B. Waite in 1893 and described on page 336 of this number of the Journal. By this method it is a simple matter to prepare strong solutions containing as much as 2 pounds of copper sulphate to the gallon. Moreover, it is possible to use large crystals instead of the more expensive and more easily adulterated pulverized bluestone. Another method, still more expeditious and superior to the old way of pouring hot water on the bluestone and stirring it till it dissolves, is to conduct steam into the bottom of a barrel containing the copper sulphate and water. With a small supply of steam, especially if under considerable pressure, the water can be heated in an incredibly short time. Besides, the current of steam issuing from the pipe sets the water and crystals in violent motion and insures a frequent change of the water in contact with crystals. In all cases where the solution is effected with the aid of heat it should be allowed to cool before being used.*

STOCK SOLUTION OF COPPER SULPHATE.

As early as 1887 the French viticulturist Ricaud† published an account of a method of making a strong solution containing a known weight of copper sulphate to each liter. This makes what is commonly

* While working at the Kansas Experiment Station in 1890, Prof. W. A. Kellerman and myself found steam conducted through a small pipe fitted with a stopcock to be a most valuable means of keeping the temperature of the water at 132° F. for treating smut of oats and wheat (see Kellerman and Swingle, Kans. Agr. Exp. Sta. Bull. No. 12, Aug., 1890, p. 49; and Georges, Burtis, and Shelton, Kans. Agr. Exp. Sta. Bull. No. 29, Dec. 29, pp. 177-178). Mr. W. C. Hewitt, manager of the Sunset Orange Company, Stanton, Fla., tells me that he finds steam invaluable in making sodium sulphide, kerosene emulsion, and other sprays. This method of heating is unquestionably the best for all who have steam available, and should be generally used by such.

† Ricaud, J. Le traitement du mildiou, la dissolution cuivreuse comparée aux autres préparations liquides (Jour. d'Agr. Prat., 51^e ann., t. 1, No. 3, Jan. 20, 1887, p. 90).

known as a stock solution. In this country Mr. Waite has used this system with great success. His method is described on page 337 of this number of the Journal. The advantages of the system are obvious; the delay occasioned by having to dissolve small amounts at a time is avoided, since a large amount can be dissolved in advance and any required number of pounds can be quickly obtained by measuring out the proper number of gallons without any operation of weighing. If steam is used for dissolving the copper sulphate, exactly the same method may be adopted as when the substance is dissolved by suspension. When it is desired to have the solution ready for use in a few hours, and neither steam nor hot water is at hand, a stock solution containing only 1 pound to the gallon can readily be made.* In no case should the copper sulphate be dissolved or stored in an iron kettle or other metal receptacle, since the copper is thrown down and other sulphates formed. A case recently came to my notice where after prolonged boiling of the copper sulphate solution in an iron kettle, the copper was all thrown down in the form of metallic scales, and the liquid on testing proved to be almost pure iron sulphate in solution. The solution can be kept a few days or a few weeks in a wooden vessel without noticeable change, but probably can not be left indefinitely without a slight loss† of strength. The vessel should of course be kept covered to prevent evaporation and to keep out impurities.

SELECTING AND SLAKING THE LIME.

Only the best well-burnt fresh stone lime should be used in making Bordeaux mixture. All powder occurring in the barrel should be looked upon with suspicion, since it is very likely to be air-slaked and consequently worthless and even dangerous to use for this purpose. In slaking, some little care is required in order to get uniformly good results. If 50 or 100 pounds are to be slaked, the amount can be placed in a barrel or other water-tight vessel. A considerable supply of water should be at hand, so that the lime will not get too dry from taking up water faster than it can be supplied. At first water should be added slowly, stirring vigorously; it should be added just as fast as it is taken up by the lime. The lumps of lime should never be allowed to project into the air for more than a few seconds. The whole slaking mass must be most thoroughly stirred or the lower portions will not be wetted at all, the upper layers absorbing all the water. It will not do to have just enough water to cause the lumps to swell and fall to a

* In this case instead of weighing out twice as many pounds as the barrel holds gallons, the same number of pounds are weighed out and suspended for solution. When all dissolved, the liquid is brought up to the required amount. This gives a solution containing 1 pound to the gallon.

† According to Clément, as quoted by Biedermann in Ladenburg, Handwörterb. d. Chemie, 6, 305, a solution of copper sulphate kept in a wooden vessel gradually deposits crystalline copper.

powder, since in this case the product is lumpy and makes a mixture of poor quality that clogs the nozzle badly. The milk of lime obtained should be of the consistency and have much the appearance of thick cream, and should be free from granules when felt between the fingers. In slaking a small amount of lime, such as 1 or 2 pounds, the mistake may easily be made of adding too much water and thus greatly retarding the action. In such cases it is best to use hot water, adding it little by little as it is absorbed. There is very seldom any difficulty in getting large amounts of lime to slake.

STOCK MILK OF LIME.

It has been found that the stock method, so valuable with copper sulphate, can be used with equal advantage for the lime. A barrel is taken, the capacity of which has previously been carefully determined, and twice as many pounds of stone lime are placed in it as it holds gallons. The lime is then slaked. If the slaking has been properly done the milk of lime will fill two-thirds to three-fourths of the space; then water is added to bring the milk of lime up to the mark. After stirring thoroughly a gallon will contain the equivalent of 2 pounds of fresh lime.* It is essential that the milk of lime be well stirred, preferably with a broad paddle. If the clear limewater be taken it will contain only about $\frac{1}{6}$ ounce of lime instead of 2 pounds. However, as the slaked lime is only a trifle more than twice as heavy as the liquid and is in an extremely fine state of subdivision, it is found easy in practice to stir up the milk of lime in a few moments, so that it is of practically uniform composition throughout. The stirring must be repeated each time a quantity is dipped out. In settling, the lime leaves a clear layer of limewater above. This contains about 1 part in 800 of slaked lime in solution and absorbs carbonic acid readily from the air, forming a pellicle over the surface. The barrels of stock lime should be kept as closely covered as possible, though if not jarred the loss from this source is certainly very small in the course of a few days or weeks. However, it is best to slake all the lime as soon as received, and in case the barrels of stock lime have to stand more than a fortnight before being used, the barrel should be headed up tightly and either the head kept covered with water or the whole buried in the ground, as suggested by Mr. Waite.

PROPER RATIO OF LIME TO COPPER SULPHATE AND MEANS OF TESTING THE MIXTURE.

The almost universal practice in this country has been to use 4 pounds of lime to 6 pounds of copper sulphate. There has been advocated of

* In case the stock milk of lime is to be used at once, it will be necessary to allow it to cool, since the heat liberated during the slaking makes it very hot, and Bordeaux mixture made hot is different in composition, settles rather quicker, and is doubtless decidedly inferior to the mixture prepared at ordinary temperatures.

late, however, the method of Patriceon,* i. e., adding the milk of lime gradually to the copper sulphate until the mixture no longer gives a brown precipitate with a solution of the yellow prussiate of potash (potassium ferrocyanide). In his bulletin on Bordeaux mixture, soon to be issued by this Division, Mr. D. G. Fairchild expresses doubt as to the value of this method. As usually recommended, it is certainly not by any means an easy method to apply, though it is often assumed to be so. If, as is usually the case, there is no means of knowing exactly how much lime is added, it is a tedious process to obtain enough without running the risk of using a great excess. As long as the amount of lime added is too small the mixture will give on adding a drop of potassium ferrocyanide solution a brown reaction plain enough to be seen against the greenish blue precipitates, but when nearly all the copper sulphate has been neutralized by the lime it is impossible to obtain the reaction without waiting for the mixture to settle and then testing the clear liquid. Well-made Bordeaux mixture settles very slowly and begins to deteriorate as it settles. Moreover, I am convinced that the mixture is not of as good quality when the lime is poured in little by little as when the proper amount is added all at once. By using the stock milk of lime described above, a definite idea is obtained of the amount of lime that has been added. Moreover, the proper ratio, when once carefully determined, can be followed without further testing in using up the rest of the two stock solutions tested. Lime must be added as long as a brown color is apparent, when a few drops of the solution is added to the mixture. A convenient way of making the test is to place a column of the mixture several inches deep in a small vial and add a few drops of the solution of potassium ferrocyanide.

Unless care be taken to add the milk of lime gradually, there is no assurance that there is not a large excess of lime in the Bordeaux mixture as prepared by Patriceon's method. However, if the clear liquid obtained by letting the mixture settle be tested with a little copper sulphate solution, an excess of lime will be shown by a bluish precipitate being formed. If it forms instantly and is very dense, there is a large excess of lime, but if it forms only after standing a few minutes and is very faint and whitish, there is only a slight excess. If in a few moments the clear liquid turns red litmus paper blue, there is an excess of lime; if blue litmus paper turns red, there is an excess of copper sulphate present. A simple method of testing for copper sulphate (one nearly as sensitive as the potassium ferrocyanide and which can be applied without waiting for the liquid to settle) is to immerse the polished blade of a steel knife in the solution and notice if after a minute or two it becomes coated with copper. If it does become so coated

*Patriceon, G. *Revue Viticole.* <*Journ. d'Agr. Prat.*, 54^e ann., t. 1., No. 20, May 15, 1890, pp. 700-704.

there is still copper in solution in the fluid. However, one of the best tests for the mixture is simply to notice the color. If too little lime is added it turns a greenish blue, if a slight excess is used the color is a beautiful sky-blue, and this is the color the mixture should show. If a great excess of lime is added the mixture takes on a slightly purplish shade of color, especially after standing a few hours. Probably the best test for the presence of an excess of lime, even when slight, is to pour some of the mixture into a broad, shallow vessel (a saucer for instance), and after a moment or two there will be formed a delicate pellicle over the whole surface. This pellicle can readily be seen if the dish is held to the light properly. It breaks when stretched and wrinkles when compressed. The amount of lime added is also a guide in the proper making of the mixture. Theoretically, $1\frac{1}{3}$ pounds of lime are required to neutralize 6 pounds of blue sulphate of copper. With ordinary lime, however, this amount is insufficient. Usually it takes twice as much to throw down all copper in solution, viz., $2\frac{2}{3}$ pounds. In general with good lime it is recommended that 3 pounds be used for every 6 pounds of sulphate of copper. This strength has been found very good for the lemon, which is injured by an excess of copper sulphate and also by any considerable excess of lime. It should never take more than 4 pounds of lime to neutralize 6 pounds of copper sulphate (unless a white or anhydrous copper sulphate has been used).

To sum up, properly made Bordeaux mixture should show a beautiful sky-blue color, and should form a faint membrane on the surface when exposed to the air for a moment in a broad dish. The clear liquid obtained on settling should give no brown color with yellow prussiate of potash solution, and should give a slightly bluish precipitate with copper sulphate solution. To obtain this result about 3 pounds of stone lime for every 6 pounds of copper sulphate should be used. Made in this way, the mixture is free from any copper in solution and also free from the greenish blue basic compounds, whose action on the plant is still in doubt. It contains a slight excess of lime very possibly beneficial to some plants, and certainly less injurious in slight excess than would be copper sulphate.

SHOULD THE MIXTURE BE MADE UP AS NEEDED OR MADE UP MORE CONCENTRATED AND DILUTED AFTERWARDS?

In using stock solutions of copper sulphate and lime, one or both may be diluted before they are mixed. I am convinced that it is of great advantage to dilute both solutions. In the mixture made from dilute solutions the chemical changes necessary to the formation are more quickly accomplished, and, best of all, the precipitates formed settle much more slowly. Ordinarily I would recommend diluting each constituent to one-half the amount the mixture is to make when completed. Then the two dilute solutions, after having been thoroughly stirred,

are poured together in the spray tank or barrel and again thoroughly stirred.* In making the mixture from diluted solutions it is best to have two vessels, each holding half as much as the tank; the proper amount of copper sulphate and lime stock can be measured out and each diluted without the trouble of measuring the water added. The superior quality of Bordeaux mixture made in this way will fully repay any extra labor of making. It does not suffice to dilute only one of the constituents.

KEEPING QUALITIES OF BORDEAUX MIXTURE.

The sooner the Bordeaux mixture is used after being made, the better. Changes in the precipitate soon begin; it eventually becomes coarsely granular, settles very quickly, and adheres very poorly to the foliage. Probably no serious degeneration of the mixture takes place inside of three or four hours, but there can be little doubt that it is decidedly of inferior quality after standing twenty-four hours.

ADDITION OF SOAP TO BORDEAUX MIXTURE.

As has been found by Galloway† and Fairchild, the addition of soap to the mixture greatly increases its wetting properties, and makes it much better for spraying plants having a waxy cuticle, and hence difficult to wet thoroughly. The exact nature of the chemical changes produced by adding soap is as yet almost unknown. The practice has been to add soap in solution until an abundant and permanent foam is produced upon stirring the mixture violently. Usually a considerable quantity of soap is required to produce this effect, about half as much as the total weight of copper sulphate and lime used. The soap should be in solution; with hard soaps it is best to shave into thin slices, dissolve in hot water, and add to the finished mixture warm. Soft soaps may be diluted and added cold.‡

* For instance, in making given stock solutions containing 2 pounds of copper sulphate or lime to the gallon, in making a mixture of the strength of 6 pounds of copper sulphate and 3 pounds of lime to 50 gallons, the procedure would be as follows: Take 3 gallons of the stock copper sulphate solution and dilute with 22 gallons of water, making 25 gallons in all; after stirring well it is ready for use. Take 1½ gallons of the stock milk of lime and dilute with 23½ gallons of water, making 25 gallons. A mark can readily be made showing to what point the barrels are filled and rendering it unnecessary to measure the water added after the first time. After stirring both the diluted solutions well, pour them at once into a tank or barrel, straining through close-meshed wire netting. The mixture should now be thoroughly stirred with a broad paddle for at least two minutes.

†Galloway, B. T. Experiments in the treatment of rusts affecting wheat and other cereals. *<Jour. of Mycol.*, vol. VII, No. 3, May 1893, pp. 195-226.

‡In this connection I would suggest that the very cheap resin soaps be given a thorough trial for this purpose. Take 2 parts of resin and 1 part of crystallized sal soda (sodium carbonate, $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$), melt together in a kettle, stirring until all lumps disappear; then dilute with about 4 parts of hot water, which will make a stock solution containing 3 pounds of the soap to the gallon. This should be diluted

SUMMARY.

(1) Copper sulphate may be dissolved very easily by suspending the crystals in a loosely woven cloth or basket near the top of a vessel filled with water or by conducting steam into the vessel through a pipe.

(2) It is most convenient to make up a stock solution containing 2 pounds of copper sulphate to the gallon.

(3) Only the best freshly burned stone lime should be used in making Bordeaux mixture. When slaked it should be free from coarse granules.

(4) Stock milk of lime containing the equivalent of 2 pounds of unslaked lime to the gallon may be readily prepared.

(5) The method of testing Bordeaux mixture with a solution of potassium ferrocyanide to determine when enough lime has been added, is difficult to apply in practice unless stock milk of lime be used.

(6) The color of the mixture is a good indication of its composition. When properly made it is of a deep sky-blue color. Such a mixture contains a slight excess of lime, and on standing a few moments in a broad, open vessel is covered with a thin pellicle of calcium carbonate. The clear liquid left after settling gives no brown color with potassium ferrocyanide solution, but does give a slight precipitate of a light bluish color with copper sulphate solution.

(7) To obtain a mixture giving the reactions noted above, about $2\frac{1}{2}$ to 3 pounds of lime will be needed for each 6 pounds of copper sulphate used.

(8) It is very much better to dilute both the copper sulphate solution and the milk of lime before mixing than to mix the strong solutions and dilute to the required quantity afterwards.

(9) The mixture begins to deteriorate within a few hours after being made and should therefore be applied as soon as possible. It should never be allowed to stand as long as twenty-four hours before using.

(10) The addition of soap to the finished mixture greatly increases its wetting properties and adds to its value for all plants with a waxy coating on the parts sprayed. The soap should be added in solution and in sufficient quantity to make the mixture foam well when stirred violently.

(11) The very cheap resin soaps are sufficiently promising to deserve a thorough trial for use with the Bordeaux mixture.

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with about 2 parts of water when added to the Bordeaux mixture. This soap costs only about $1\frac{1}{2}$ cents a pound in large amounts, while whale-oil soap costs about four times as much, and ordinary good hard soap costs five to twelve times as much. From a few preliminary trials made, it seems to be even better than ordinary soap to make a foam with Bordeaux. Albert Koebele found a similar resin soap to be a good insecticide for some haustral insects (see Annual Reports of the Commissioner of Agriculture for 1886 p. 558; 1887, p. 146; and 1888, p. 130).